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HAZARDOUS GASES AND SUBSTANCES FOUND IN UNDERGROUND MINE AIR

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by

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ABSTRACT

Air in underground mines contains contaminants including gases such as carbon monoxide, nitrous oxides, sulphur compounds, methane and carbon dioxide, and solids in the form of dusts, smokes or fumes from various mining activities such as diesel, load-haul-dump operations and blasting. Emanations from the strata can also be a substantial source of contamination.

Threshold Limit Values (TLV's) and flammability limits have been established for various toxic and/or inflammable substances. Canadian regulatory agencies use standards set in the United States by the American Conference of Governmental Industrial Hygienists (ACGIH). Although the ACGIH considers these TLV's as being guidelines, adherence and compliance to such guidelines should ensure a safe workplace for mine employees.

Dilution by ventilation helps maintain the concentration of contaminants to a safe level. Preventive measures such as proper use of explosives and regular maintenance of diesel equipment also help to provide a better working environment.

In this report details are given as to the source, toxicity and/or inflammability of some undesirable substances found in underground mines. Means of control are also described.

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SUBSTANCES ET GAZ NOCIFS EN SUSPENSION DANS L'AIR DES MINES SOUTERRAINES

par

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RÉSUMÉ

L'air des mines souterraines contient des impuretés y compris des gaz comme l'oxyde de carbone, les oxydes azoteux, les composés sulfureux, le méthane, le bioxyde de carbone et des solides sous forme de poussière, fumées ou vapeurs qui se dégagent au cours de certaines activités telles l'utilisation d'équipement diésel, les manoeuvres de chargement, de déversement et de sautage. Les émanations qui s'échappent des couches géologiques peuvent également constituer une source importante de pollution.

La concentration maximale admissible (CMA) en ce qui a trait à la pollution et les limites quant à l'inflammabilité de diverses substances toxiques et/ou inflammables ont été fixées. Les organismes régulateurs du Gouvernement canadien utilisent des normes qui ont été établies aux États-Unis par la American Conference of Governmental Industrial Hygienists (ACGIH). Bien que la ACGIH ait fixé ces normes en tant que lignes directrices, une adhésion à celles-ci et l'observation des règlements devraient assurer la sécurité des mineurs dans leur milieu de travail.

La dilution des vapeurs nocives par la ventilation aide à maintenir la concentration des impuretés à un niveau sûr. Des mesures préventives comme, par exemple, l'utilisation appropriée des explosifs et l'entretien régulier de l'équipement diesel permettent également d'assurer de meilleures conditions de travail.

Dans ce rapport, l'auteur présente des renseignements particuliers concernant la source, le degré de toxicité et/ou d'inflammabilité de certaines substances indésirables en suspension dans l'air des mines souterraines de même qu'une description des méthodes de contrôle.

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INTRODUCTION

The standard atmosphere is made up of 78.08% nitrogen, 20.95% oxygen, 0.93% argon, 0.03% carbon dioxide and a 0.01% of other gases. The above percentages are for dry air whereas normally water vapour accounts for up to 3% of the air content. When ventilation is used to force air through an underground mine, several changes occur in the proportion of its constituents and several impurities are also added. Ordinarily, oxygen would be reduced, carbon dioxide content would increase and the water vapour content may increase or decrease. Dust and particulate contaminants are added as a result of mining activity. Harmful gases are also produced underground which will change the composition of the air.

The degree to which air is contaminated generally depends on the gas content of the strata as well as its chemical reactivity and the mining methods employed. The volume of air ventilating the mine will also have an influence on the quality of air. In this report, the guidelines used to regulate the allowable concentration of harmful contaminants are defined, and these contaminants are examined from the point of view of their toxicity, inflammability, physical parameters, Threshold Limit Values (TLV) for exposure, means of detection and sources. Finally, special attention is given to gases and particulates produced by diesel engines and other operations carried out routinely in underground mines.

GUIDELINES FOR EXPOSURE TO TOXIC SUBSTANCES

Canadian regulatory agencies use American standards as guidelines for exposure to toxic substances in the workplace. The standards are referred to as TLV, and they are listed and updated in a publication of the American Conference of Governmental Industrial Hygienists (ACGIH) (1). TLV's are meant

to be used as guidelines and as they presently stand. they are thought to be the limit of exposure to workers day after day without adverse effects on their health. TLV's are usually expressed as parts per million (ppm) or milligrams of a given contaminant per cubic metre of air (mg/m^3).

Some substances are very toxic and will cause death in a few hours if a certain concentration is exceeded. In some instances. even a few minutes of exposure to such substances may be fatal. Other substances. however. are also dangerous. but much less potent. Excursions beyond what is thought to be a safe level may be allowed without seeming to endanger workers' health. In association with these levels. three types of TLV's are defined. These are the time weighted average (TLV-TWA): the short-term exposure limit (TLV-STEL): and the ceiling Threshold Limit Value (TLV-C).

THE CEILING TLV

For substances such as nitrogen dioxide. even very short-term exposures to high concentrations may be dangerous or even fatal. For this reason. TLV-C values are not to be exceeded under any circumstances and for any exposure time. no matter how short.

THE SHORT-TERM EXPOSURE LIMIT TLV

Short-term exposure limits (TLV-STEL) are permitted for some toxic substances. The STEL values are the maximum concentration to which a worker may be exposed for a period of up to 15 minutes. provided that there be no more than four such periods in one 8-hour shift. and that at least one hour has elapsed between the high concentration exposure periods. STEL-TLV's are given for substances to which higher exposure will not cause lower work efficiency. increase the risk of accident. or cause irritation and tissue damage. It should go without saying that the time weighted-average TLV for the shift is to be respected in all cases.

THE TIME-WEIGHTED AVERAGE TLV

THE TIME-WEIGHTED AVERAGE TLV

Since the concentration of toxic substances may vary substantially in a working shift, it is not practical to set TLV's which cannot be exceeded at any given time. For this reason excursions beyond TLV-TWA's are permitted as long as the TLV-C (if one exists) is not exceeded.

The TLV-TWA is the time-weighted average concentration of a toxic substance to which a worker may be exposed in the course of a normal 8-hour shift. Excursions beyond the TLV-TWA are tolerated as long as the guidelines set by the TLV-STEL and the TLV-C (as they apply) are not violated, and also as long as the TLV-TWA is not exceeded in an 8-hour shift.

When several toxic substances are present, the exposure is to be considered as additive (as long as the contaminants present have similar toxicity levels). For example, if n contaminants are found in a given environment, then the following rule applies:

$$\sum_{i=1}^{n} \frac{C_i}{TLV_i} \qquad \text{Eq 1}$$

In Equation 1, C_i and TLV_i are the time weighted average concentration and the Threshold Limit Value (TLV-TWA) for contaminant i, respectively. If the above summation exceeds unity, then the TLV for the mixture would have been violated.

BIOLOGICALLY INERT SUBSTANCES

Substances such as methane, helium and hydrogen are not considered toxic, and as such cannot have TLV's assigned to them. These substances will, however, become suffocants if allowed to accumulate to concentrations where the percentage of oxygen in air is reduced significantly. Under standard pressure and temperature conditions, oxygen should account for at least 18% of the air mixture. Below 16%, oxygen deficiency symptoms progressively include laboured breathing, accelerated pulse, dizziness, buzzing in the ear, and loss of consciousness and death for levels below 6%.

In a human lung the surface available for gas/blood interaction is estimated at over 50 m^2 (2). For this reason, gases are readily absorbed into the blood stream at a rate proportional to the partial pressures of these gases. Factors affecting the process are the temperature (which will not vary significantly in the human lung), and barometric pressure (which can change significantly in underground mines). While intake routes and mechanisms for gases are fairly well known, the same is not true of dusts, fumes and smokes.

Although large dust particles may be irritating to the nose, throat, eyes and skin, particles less than 7 mm in size are called respirable and will deposit at various levels of the respiratory tract depending on size. Several mechanisms will cause attachment to lung surfaces, including gravitational sedimentation and inertial impaction for dense particles as well as interception and diffusion. Dusts generally found in underground mines are not much of a threat in the short-term, but through physical and chemical interaction with lung tissue will, in the long term, increase the risk of cancer (e.g., diesel particulate emissions), or other forms of pneumoconiosis (e.g., silica from airborne quartz dust). Toxic dusts can also be ingested, either directly swallowed in the saliva, or in the mucus that is swept back from the tracheabronchial tree.

For the picture to be complete, it should be mentioned that some toxic substances are readily absorbed through the skin. Nitroglycerin is absorbed in this fashion. The phenomenon is well known to experienced miners as headaches often come from handling explosives without proper protective equipment.

HAZARDOUS SUBSTANCES FOUND IN UNDERGROUND MINES

The following section is a list of substances that are a threat in underground mines. These substances are either categorized as toxic (in which case the TLV's will be given), or they may represent a danger as suffocants, or may be inflammable and/or explosive under specific conditions. Table 1 lists these gases along with TLV's and flammability limits, where applicable.

CARBON MONOXIDE (CO)

This is an extremely toxic, colourless, tasteless and odourless gas. It is slightly lighter than air with a specific gravity of 0.97. The danger with CO comes from its high affinity to hemoglobin in the red blood cells. As little as 500 ppm of CO in air can cause death within three hours. By then 50% of the blood's hemoglobin is saturated with the gas. Carbon monoxide can be formed as a result of incomplete combustion in diesel engine exhaust, after blasting operations, and as a result of mine fires underground. Decaying organic matter, such as timber in shut down areas, is another possible source of carbon monoxide. The gas is inflammable when it forms between 12.5% and 74% of the air mixture.

The TLV for carbon monoxide is 50 ppm. In the past, canaries or mice were brought underground to detect CO accumulations. The animals became unconscious if they were exposed to 0.06% CO concentrations. Now, change of colour or colorimetric tubes are used. These contain a chemical gel whose colour changes according to the carbon monoxide concentration. These devices have an operational range that lies between 10 and 1000 ppm. Disadvantages to this method include the fact that the colour change is hard to assess in dark areas (underground), and other substances, such as nitrogen dioxide, do in some cases interfere with the reaction. Another detector device called the length of stain tube eliminates the problem of assessing a change of colour.

Table 1 - Hazardous gases found in mines
(reproduced from reference 3)

Gas	Symbol	TLV (ppm)	Flammability Limits (%)	Hazard
Carbon monoxide	CO	50	12.5-74.0	Highly toxic
Nitric oxide	NO	25	-	Highly toxic
Nitrogen dioxide	NO_2	5	-	Highly toxic
Hydrogen sulphide	H_2S	10	4.0-44.0	Toxic
Sulphur dioxide	SO_2	5	-	Toxic, irritant
Carbon dioxide	CO_2	5000	-	Asphyxiant
Methane	CH_4	-	5.0-15.0	Explosive, asphyxiant
Hydrogen	H_2	-	5.0-75.0	Flammable
Nitrogen	N_2	-	-	Asphyxiant
Ozone	O_3	0.1	-	Highly toxic

but these also react with other airborne contaminants. More sophisticated analog instruments exist that operate on the principle of heat of reaction of oxidizing carbon monoxide to carbon dioxide. A thermistor is used to measure the heat produced which is proportional to the amount of CO present. This instrument will measure CO in the range of 0 to 500 ppm. Another analog instrument senses a change of colour from a substrate treated chamically and evaluates this change with the help of a photoelectric system.

OXIDES OF NITROGEN (NO AND NO_2)

Oxides of nitrogen are very harmful to the respiratory system. Nitrogen dioxide is almost colourless in low concentrations (but still very toxic) and has a reddish-brown colour when found at higher concentrations. It is heavier than air and its presence may be suspected when blasting fumes are detected. Nitrogen oxides are toxic because they form very corrosive acids that affect lung tissues as they react with the moisture therein. The gases are extremely irritating to the throat and may cause edema of the lung which can be fatal. Nitrous oxides are usually produced in diesel exhaust and blasting operations, but can also be found in welding fumes.

The TLV's for NO and NO_2 are 25 ppm and 5 ppm. respectively. Both compounds are also non-flammable. Monitoring of nitrogen oxides is conducted with length of stain tubes. These devices have a shelf life of two years at room temperature. Relative humidity, temperature and other gases can interfere with the readings.

HYDROGEN SULPHIDE (H_2S)

This colourless toxic gas has the odour of rotten eggs. Exposure to hydrogen sulphide does, however, dull the sense of smell, so that one cannot rely on smell to adequately assess the danger. The specific gravity of H_2S is 1.191 (denser than air). The compound can be rapidly fatal at concentrations greater than 600 ppm. Hydrogen sulphide is liberated from the strata as a

result of chemical reactions with sulphide ores. It is also produced when blasting these ores. Emanation of the compound may occur in abandoned mine workings, where it may be formed by rotting organic substances. The compound when found in air is inflammable in a wide range of concentrations (4 to 44%).

The TLV for hydrogen sulphide is 10 ppm and it is also detected by means of length of stain tubes. These tubes usually measure H_2S in the range of 1 to 1000 ppm.

SULPHUR DIOXIDE (SO_2)

Sulphur dioxide is a colourless, suffocating gas. It is an extreme irritant and is much heavier than air. It is readily formed in blasting operations and fires in mines with a high sulphide ore content. It is easily detected by its very pungent sulphurous smell. Sulphur dioxide is non-flammable and has a TLV of 5 ppm. It can be detected with length of stain tubes in a range of 1 to 1000 ppm.

CARBON DIOXIDE (CO_2)

Carbon dioxide, a colourless, inert gas, is denser than air (specific gravity at 1.529). This gas though non-toxic, is hazardous as an asphyxiant. When found in concentrations in excess of 10%, it deprives the body of oxygen to the point where an individual at rest can be in grave danger within a few minutes. Carbon dioxide is produced by internal combustion engines, organic decay, strata emissions, blasting operations and mine fires. It has a TLV of 5000 ppm and is also detected with length of stain type tubes which may be sensitive to concentrations beyond 100,000 ppm.

METHANE (CH_4)

Methane has been called marsh gas and fire damp. It is lighter than air (specific gravity of 0.559) as well as being colourless, odourless and tasteless. Methane is non-toxic but it may act as an asphyxiant (O_2 deficiency). Methane is extremely inflammable and explosive in a range of

concentrations between 5 and 15%. This gas is notorious for having been the cause of large scale explosions in coal mines which over the years have resulted in several thousands of fatalities. Methane diffuses from the strata and is often encountered in hard rock mines. Methane may be detected with flame safety lamps at concentrations of up to 2 or 3%. It can also be monitored with detector tubes or meters within a similar range.

HYDROGEN (H_2)

Hydrogen is a colourless, odourless and tasteless gas with a specific density of 0.069. Since it is very much lighter than air it will tend to accumulate along the back in certain poorly ventilated areas. It is non-toxic, but will form an inflammable mixture in air over a wide range of concentrations (5 to 75%). The gas is rarely found in underground mines at concentrations where it might be a threat, but it may accumulate in hazardous quantities at locomotive/tram battery charging stations. The gas can be monitored in a range of 0.5 to 3% with the help of detector tubes.

NITROGEN (N_2)

Nitrogen is an inert colourless, tasteless and odourless gas. In a normal atmosphere it forms about 78% of the air mixture. It is non-toxic and is not a threat unless allowed to accumulate to levels where oxygen is appreciably depleted.

OZONE (O_3)

This gas has a distinctive smell and is very toxic, even at low concentrations. It attacks the respiratory system and is rapidly fatal (30 minutes) at 50 ppm. The TLV for ozone is 0.1 ppm. It may accumulate around electrical equipment and in areas where electrical welding is being performed. Ozone is monitored with detector tubes.

DIESEL EXHAUST IN UNDERGROUND MINES

THE DIESEL ENGINE

One of the basic differences between gasoline and diesel engines is that, in the former, a variable quantity of a constant fuel/air mixture is injected into the cylinders, where as in the latter, more fuel is injected for a constant amount of air when more power is needed. Because of this, powerful diesel engine equipment is very attractive to the mining industry as the machinery is simple and easy to maintain. On the negative side, however, diesel engines produce a lot more pollutants than comparable gasoline engines as a result of incomplete combustion when richer fuel mixtures (higher fuel/air ratio) are being injected. The average diesel engine uses a fuel/air ratio that ranges between 0.01 and 0.042. At high mixing ratios, a diesel engine may produce as much as 100 times more particulate matter than a gasoline engine.

TOXIC SUBSTANCES FROM DIESEL EXHAUST

Diesel fuel is a mixture of hydrocarbons, and as such is made up of about 84% carbon, 15% hydrogen and less than 1% sulphur. Assuming a perfectly atomized and homogeneous fuel/air mixture inside the cylinder and a sufficient amount of oxygen throughout ignition, then an ideally complete combustion would yield 70% carbon dioxide, 29% water and some sulphur dioxide. In practice, however, complete combustion is not achievable, partly because the ideally homogeneous fuel/air mixture is not easily produced. In any particular unit volume within the combustion chamber, prior to ignition, there is a fuel/air mixture that is suitable for combustion. There are also fairly large droplets of liquid fuel which upon ignition will produce small particles, almost all of which are in the respirable range. These small carbon particles are formed along with some viscous hydrocarbons and other

compounds. Hundreds of organic compounds have been identified in diesel exhaust. Among these, a class of Polynuclear Aromatic Hydrocarbons (PAHs) include a known carcinogen called benzo(a)pyrene. Eye and lung irritants, such as aldehydes and phenols are also found in diesel exhaust.

Toxic gases formed in diesel exhaust are produced as a result of high temperature and pressure conditions and/or lack of oxygen causing incomplete combustion. Carbon monoxide is produced when oxygenated organic compounds are further oxidized. If more oxygen is available, CO will be transformed to CO_2. At high temperatures and pressures, nitrogen and oxygen combine to form oxides of nitrogen. As engine load increases, so does the temperature inside it. Hence, oxides of nitrogen will be produced in greater quantity at higher load operating modes. Oxidation of the sulphur compounds in the fuel produces sulphur dioxide.

CONTROL AND REMOVAL OF NOXIOUS SUBSTANCES IN DIESEL EXHAUST

When referring back to the products of complete combustion of diesel fuel, it seems that the ideal way to control emissions would be to achieve as complete a combustion as possible inside the engine's cylinder. Total combustion of hydrocarbons in the fuel is not possible, but steps can be taken to substantially improve the quality of exhaust. Proper adjustment of the fuel-injection system is important, as it ensures that fuel and air are mixed in a proper ratio and injected in a uniform spray. Worn engine parts (valves and rings) will also contribute to excessive exhaust pollutants being produced. Derating of diesel engines for use underground (allowing no more than a certain quantity of fuel to be mixed per unit mass of air) is important in reducing the amount of thermally degraded hydrocarbons.

Apart from controlling noxious products, diesel exhaust contaminants may be removed to a certain extent. Catalytic converters are used to oxidize CO and some portion of unburnt hydrocarbons to CO_2. Sulphur dioxide is also

oxidized to form SO_3. Upon cooling, the SO_3 combines with water vapour to form sulphuric acid. It seems however, that catalytic converters do not effectively reduce the mass of particulates produced. Other types of exhaust conditioning devices have been developed. Among these, ceramic exhaust filters have been tested in Canada (4). So called water scrubbers or similar devices using scrubbing liquors other than water can be used to effectively remove the sulphuric acid mists.

NOXIOUS FUMES AND GASES FROM EXPLOSIVES AND MINE FIRES

EXPLOSIVES

In underground mines, only class 1 explosives are allowed. Class 1 explosives are defined by the U.S. Bureau of Mines as agents which when 161 cm^3 (1 1/4 inch diameter and 8 inch length cartridges) of the material is detonated, will produce less than 0.0045 m^3 (0.16 cu ft) of toxic gases. Traditionally the Bichel Gauge method has been used to determine the amount of toxic gases produced; but several drawbacks exist that make this method somewhat unattractive. Among these are the fact that oxides of nitrogen cannot be measured, and also that the test cannot be performed on some modern explosives because the detonating mechanisms cannot be accomodated by the test (5). In view of this, it has been suggested by several authorities, that fumes tests be performed in situ and/or under conditions that best reproduce actual blasting operations (5,6).

The main toxic gases produced by underground blasting are carbon monoxide, nitrogen oxides and hydrogen sulphide. Blasting in sulphide ores can also produce a substantial amount of sulphur dioxide. Blasting operations in such ores produce sulphide dusts which are ignited in the process thus forming sulphur dioxide. The problem is well known and methods of controlling these have been tested and are documented (7).

MINE FIRES

Fires in underground mines can produce large quantities of carbon monoxide, carbon dioxide and sulphur dioxide, all of which are either toxic or asphyxiating gases. But fires underground may produce a vast amount of other gases depending on what materials are supporting combustion. The gases and chemicals produced by these fires can be extremely toxic and even small fires may cause fatalities.

Tests conducted in U.S. laboratories (8) show that in a mine fire, a considerable amount of toxic fumes could be produced from the thermal degradation of some fire resistant conveyor belts, brattice cloth and wire insulators. In these tests, a fair amount of CO was measured, but hydrogen chloride was also found to emanate in concentrations that could cause serious problems in some circumstances. Some nitrogen dioxide was also produced. Thermal degradation of other substances, such as solvents and hydraulic fluids, may produce highly toxic fumes. Solvents are used extensively in underground mechanic shops for degreasing, and hydraulic fluids are also stored in large quantities in such areas. When solvents were tested in U.S. laboratories (9), thermal degradation showed the formation of phosgene (TLV = 0.4 mg/mg), and hydrochloric acid (TLV = 7 mg/m^3). Similar experiments performed on hydraulic fluids produced a variety of toxic substances depending on the fluid tested. In most cases, carbon monoxide and acrolein (TLV = 0.1 ppm) were produced.

OTHER SOURCES OF TOXIC SUBSTANCES

Emissions from the strata can lead to problems in certain cases. These gases are a combination of toxic, inflammable and/or asphyxiating. They can escape gradually and accumulate in poorly ventilated or barricaded areas. They can also be released suddenly in blasting operations or when conducting

exploratory drilling. These gases include methane, hydrogen, nitrogen, carbon dioxide and sulphur dioxide.

Old workings can be dangerous areas and proper care must be exercised before entering. First, oxygen may have become depleted by dilution from other gases. Oxidation of ores, such as sulphides, may also have reduced the oxygen concentration. The decaying of organic matter in hot and humid environments requires oxygen as well. Carbon monoxide can be produced by oxidation of carbonate ores. Hydrogen sulphide may be found in old working areas where the leaching action of acid waters on sulphide ores is taking place. Methane may be produced by decaying organic matter or may emanate from the strata.

Compressed air drills and other machinery produce a very fine oil mist. The ACGIH recommends a TLV of 5 mg/m^3 for such irritants. These may cause nausea and affect the respiratory system. Battery charging stations underground produce hydrogen gas which if allowed to accumulate could become a threat because of its wide range of inflammability. Welding operations are a source of ozone and also produce very noxious metal oxide fumes. Cement grouts used for support purposes in mines are made shrink-resistant by the addition of metallic powders. These grouts, when setting, become bulkier by the action of the metal additives. This is achieved by oxidation of these metals (oxygen depletion), or by the formation of hydrogen bubbles in the grout (hydrogen production). It should be noted that for most applications underground, grouting should be a very small source of problems in well ventilated aras, as the area of interface (air/grout) is usually small in comparison with the amount of grout used.

CONCLUSION

Many hazardous substances are found in underground mines. The ACGIH has established TLV's for most of these substances. Although the ACGIH considers that these Threshold Limit Values should be used as guidelines only, adherence and compliance should ensure a safe workplace for mine workers.

In most cases, ventilation (dilution) is the most efficient way to bring the concentration of hazardous materials down to a safe level. The problem, however, can also be tackled at the source. Proper use of explosives will cause a lesser amount of noxious fumes to be produced. Rigorous scheduled maintenance of diesel engine equipment, as well as use of low sulphur content fuel would be desirable. More work is needed in order to assess the relative benefits of catalytic converters, scrubbers and dilutors on diesel equipment in order to establish what the optimal exhaust conditioning equipment should consist of.

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